

Examining bonding electrons at different oxygen sites in Sr_2RuO_4

One of the most burning questions in contemporary solid-state science is the nature of the mechanism driving superconductivity in the high-temperature superconductors (HTSCs), first discovered more than a decade ago. Some of these ceramic-oxide materials with complex compositions and structures retain their superconductivity at temperatures up to 125K. The Nobel-prize-winning model (Bardeen-Cooper-Schrieffer theory) developed for conventional metallic superconductors is not applicable, but no one yet knows exactly what the alternative is. Clues come not only from direct examination of the materials themselves but also from studies of related materials with similar composition and structure.

A multi-institutional group working at the ALS and at the Photon Factory in Japan has taken a step in this direction by demonstrating the ability to selectively examine the electronic structure of bonding electrons associated with oxygen in two different sites in the crystal structures of the strontium

ruthenate compounds Sr_2RuO_4 and $\text{Sr}_2\text{RuO}_{4.25}$. For one oxygen site, the experimenters were able to demonstrate hybridization (mixing) between electronic states of oxygen and ruthenium. The nature of the hybridization is different from that occurring in HTSCs and results in a different type of chemical bond. Their results also show that these compounds are indeed “extended-electron” systems, thus adding a new dimension to research in transition-metal compounds.

The salient features in the strontium ruthenate crystal structure are planes comprising only ruthenium and oxygen atoms. Although there are interactions between planes, they are much weaker than those between electrons in the same plane, so that the systems are quasi-two-dimensional. There are also oxygen atoms outside the planes (apical oxygens). Owing to the different chemical environments for oxygen in these two types of sites [O(1) in the planes and O(2) outside], the photon energies to excite oxygen 1s electrons

into 2p states are slightly different (chemical shift). The group was able to distinguish oxygen atoms in the two inequivalent sites spectroscopically by exploiting the chemical shift to selectively excite oxygen in the O(1) and O(2) sites. Their experiments combined soft x-ray absorption (total-fluorescence-yield method) and soft x-ray emission.

The chemical shift manifested itself as an excitation-energy dependence of the O K- α x-ray emission spectrum (2p \rightarrow 1s transition) of Sr_2RuO_4 near the threshold for exciting x-ray emission; that is, the shape of the emission spectrum changed as the exciting photon energy was stepped at intervals above the threshold. These spectra nicely matched the atom-decomposed partial density of electron states for the two oxygen sites calculated by theorists. Comparing the spectra with angle-resolved photoemission spectra of Sr_2RuO_4 , which can distinguish ruthenium electron states of different symmetry [4d(t_{2g}) and 4d(e_g)], and with ruthenium $N_{2,3}$ emission

(4d \rightarrow 4p transition) spectra, the group determined that the O(1) 2p states are mixed with d(t_{2g}) ruthenium states, thereby forming hybridized π bonds..

Strontium ruthenate is a low-temperature superconductor (critical temperature $T_c = 1.5$ K) that is structurally similar to the cuprate HTSCs, such as $\text{Sr}_x\text{La}_{2-x}\text{CuO}_4$ and $\text{YBa}_2\text{Cu}_3\text{O}_{7-\delta}$, in which Cu-O planes replace the Ru-O planes. Not only may measurements such as these shed light on HTSCs, but similar experiments apply equally well to a far larger class of so-called “complex materials,” again often oxides with elaborate compositions and structures and an immense variety of entrancing and possibly technologically useful properties. For example, colossal magnetoresistance (CMR) compounds exhibit up to 100,000 times larger changes in electrical resistance in an applied magnetic field than occurs in the merely giant magnetoresistance (GMR) materials now coming into commercial use as read heads in high-density magnetic data-storage systems.

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SITE-SELECTIVE X-RAY EMISSION SPECTROSCOPY

Examining Bonding Electrons at Different Oxygen Sites in Sr_2RuO_4



- **Complex oxide compounds are at the frontier of solid-state physics**
 - *High-temperature (high- T_c) superconductors*
 - *Colossal-magnetoresistance materials*
 - *Strongly correlated electron phenomena*
 - *Low-dimensional systems*
- **Soft x-ray emission spectroscopy examines electronic structure**
 - *Measures density of occupied quantum states with electron energy*
 - *Element selective by excitation of core electrons at characteristic energies*
 - *Site selective by shifts in excitation energy with atomic environment*
- **Strontium ruthenate transition-metal oxide compounds**
 - *Non-copper containing analog of high- T_c cuprate superconductors*
 - *Low-temperature superconductor ($T_c = 1.5\text{K}$)*
 - *Possible clues to mechanism of high-temperature superconductivity*



SITE-SELECTIVE X-RAY EMISSION SPECTROSCOPY

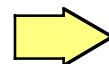
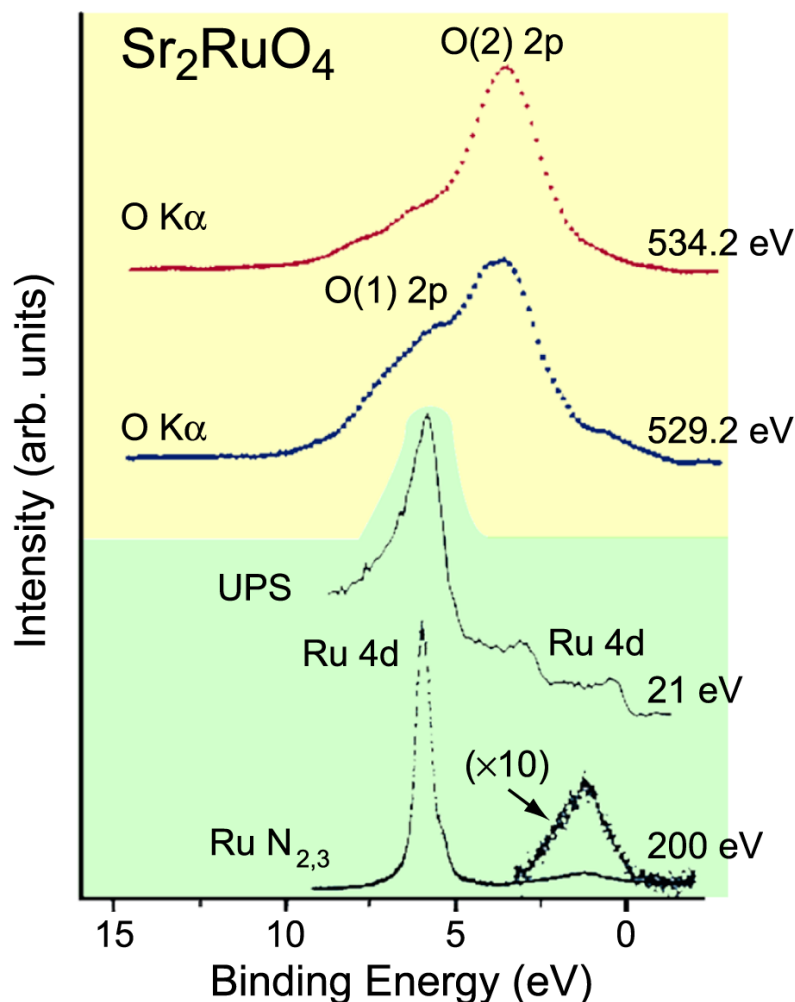


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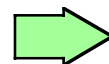
- **Key features of strontium ruthenate layered Perovskite structure**
 - *Planes containing only ruthenium and oxygen atoms*
 - *Additional oxygen atoms out of plane*
- **Oxygen x-ray emission spectra depend on excitation energy**
 - *Distinguish between in-plane and out-of-plane oxygen sites*
 - *In-plane oxygen spectra have extra features*
- **Oxygen and ruthenium emission spectra have features at same binding energies**
 - *Evidence for hybridization of in-plane oxygen and ruthenium states*
 - *Angle-resolved photoemission identifies electron states involved*
 - *Shows strontium ruthenate is an extended, not localized, electron system*
 - *Band-structure calculations verified*

SITE-SELECTIVE X-RAY EMISSION SPECTROSCOPY

Examining Bonding Electrons at Different Oxygen Sites in Sr_2RuO_4



Soft x-ray emission spectra from oxygen in in-plane O(1) and out-of-plane O(2) sites are distinctly different



Matching structure at -6 eV in the spectra and in the O(1) ruthenium spectrum demonstrate hybridization